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Cadmium levels in coastal and estuarine waters of Western Australia

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Abstract

The stable isotope dilution technique has been used to measure the cadmium concentration in 30 coastal and estuarine water samples from 16 locations around the Western Australian coast, from Albany in the south to Pardoo Station in the north. A base-line value of 0.013 ppb ($\mu g\ kg^{-1}$) cadmium for coastal sea water has been established, and this result compares favourably with overseas studies. It is pleasing to note the minimal levels of contamination caused by industry, and in most cases it seems that the nature of the environment controls the cadmium levels present.

Introduction

Cadmium was recognized many years ago as a highly toxic element. However it was not until comparatively recently that concern was expressed over the possible effects to human health of exposure over long periods to low concentrations of cadmium. This situation has developed because of the increasing technological use of cadmium (Cox 1974). Ingestion from food or water, and inhalation from the atmosphere are the major routes by which cadmium enters the body.

Cadmium is used by industry in electroplating, in pigments and chemicals, as a plastics stabiliser, in alloys and solder, in making batteries, photocells and in pesticides. Cadmium minerals are found in conjunction with zinc ores because of the geochemical similarity of the two elements, and hence a major source of cadmium in the environment is the zinc industry. Thus, in addition to zinc refining, there are a number of processes which involve cadmium including galvanizing iron and steel, making brass and other alloys and in the production of zinc oxide.

The World Health Organisation (WHO 1963), has declared that the maximum advisable concentration limit for cadmium in drinking waters is 10 ppb ($\mu g\ kg^{-1}$). Long term exposure to cadmium-contaminated food and water has been found to induce a bone disease in members of a small community in Japan, who live in the Jintsu region situated on a river heavily polluted by mining wastes (Singhal *et al.* 1975).

A variety of cadmium minerals exist in nature and these are soluble in excess aqueous salt solutions; many cadmium compounds are also soluble in fresh water (Cox 1974). Williams and David (1973) have shown that the cadmium content of phosphatic fertilisers and superphosphate used on Australian pastures ranges from 27 to 90 ppm ($mg\ kg^{-1}$). Thus cadmium can be transferred to natural waterways, and hence find its way to estuaries and the oceans.

Rosman and De Laeter (1976), have measured the concentration of cadmium in two river systems in Western Australia, and shown that the content is approximately one hundredth of the WHO recommended value. This data may therefore serve as a basis for comparison with cadmium concentrations in waterways in other parts of the world. De Laeter *et al.* (1976), examined the cadmium content of rural tank water and have shown that in most cases the concentration is less than 1 ppb.

There is considerable interest in the fate of heavy metals in estuarine and coastal environments, and several studies have been carried out to determine the effects of discharging effluents containing heavy metals into estuarine waters. It has usually been assumed that such effluents are rapidly dispersed in the open sea (Butterworth *et al.* 1972). In assessing the impact on the environment of effluent containing cadmium, it is necessary to know the concentration of cadmium that would have been present in the absence of waste material. However these background levels are poorly documented in the literature, and the present study was undertaken to provide a set of base-line values for coastal and estuarine waters around the Western Australian coast, similar to the base-line values determined by Rosman and De Laeter (1976) for river systems.

Experimental procedure

It is quite likely that much of the published work on environmental cadmium is inaccurate, particularly where the content is at the sub-ppb level. The present project has used the stable

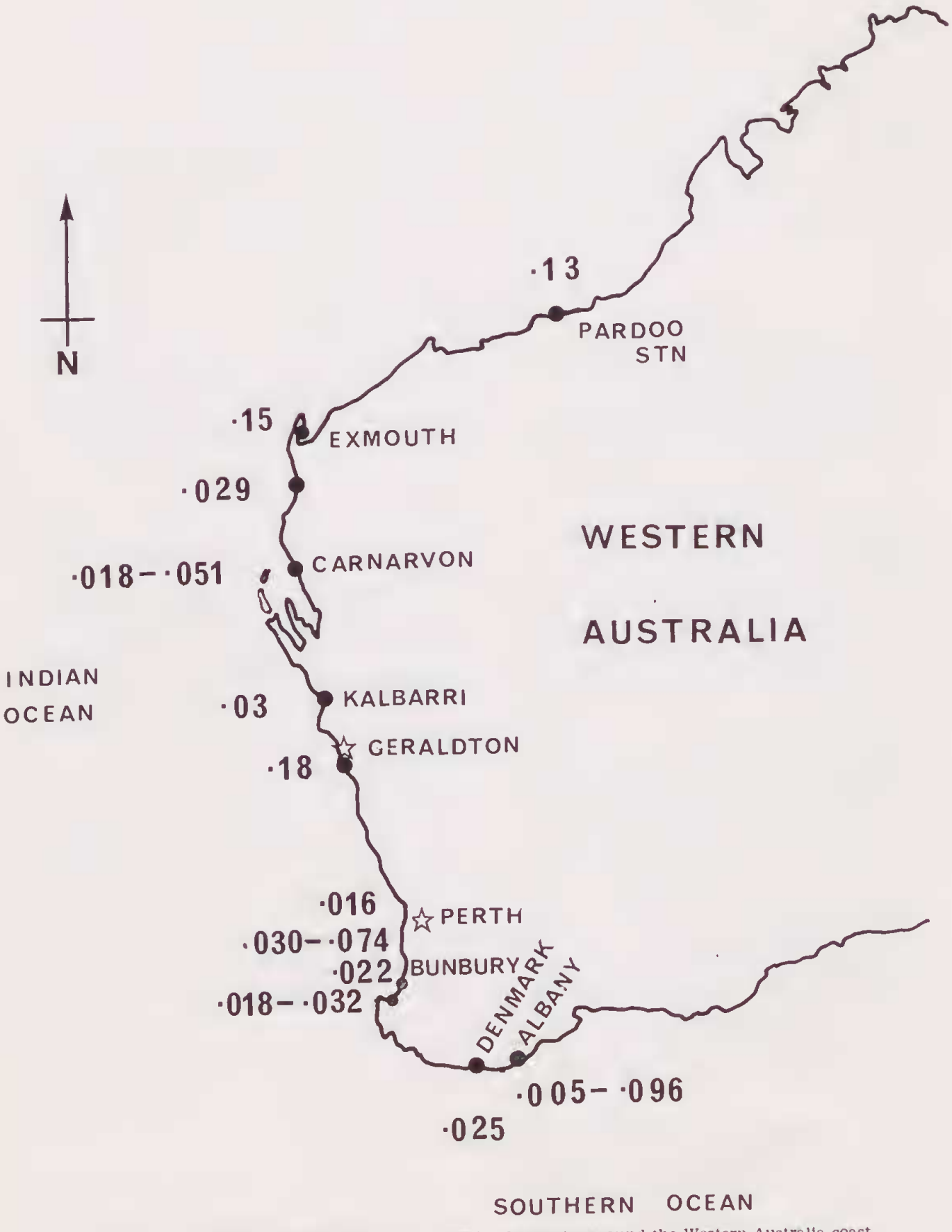

Figure 1.—Cadmium concentrations (in $\mu g\ kg^{-1}$) of seawater around the Western Australia coast.

isotope dilution technique to measure the eadmium eontent of oeean water along the eoast of Western Australia. Because of its exeellent sensitivity, high aeeuraey and preeision, the isotope dllution teehnique is ideally suited to the analysis of cadmium in the environment. The sensltivity of thls teehnique for cadmium in aqueous samples is 0.003 ppb, and the absolute aeeuraey is better than 10% at the sub-ppb level.

Water samples were eolleeted in high density polyethylene eontainers, sinee it has been shown that polyethylene does not absorb eadmium from aqueous solutions and exhibits a low blank (Struempler 1973). The bottles were eleaned with high purity 6M HCl to remove any resldual eontamination. They were then washed thoroughly wlth quartz-distllled water, some of whieh was left in the bottle until the sample was eolleeted. Before the sample was taken, the bottle was emptied, rinsed with sea water and filled with water taken near the surfaee. An unfiltered 200 g aliquot of eaeh water sample was aeidified and spiked with an aeeurately known weight of isotopieally enriehed ^{111}Cd traeer. After ensuring that the spike and sample were well mixed, the eadmium was ehemieally extraeted by ion exehange. Full details of the ehemieal extraetion proeedure are given by Rosman and De Laeter (1977).

After the eadmium was extraeted it was mounted in the souree of a 30.5 em radius, 90° magnetie seetor field, solid souree mass speetrometer. From the measured isotopie ratios the eoneentration of eadmium ln each sample was determined. It was found necessary to make a blank eorreetion of approxlmately 2×10^{-9} g for eaeh sample. A blank was ineluded with eaeh bateh of samples undergoing ehemieal proeessing.

Results and discussion

Water samples were collceted from 16 loeations around the Western Australian eoast, from Albany in the south to Pardoo Station in the north (Fig. 1). Multiple sampling was earried out at 7 of these loeations, making a total of 30 samples available for analysis. For almost every sample, duplieate analyses were made to provide an indieation of the reproduelbility of the proeedure. Table 1 llsts the loeation and eadmium eoneentrations of the 30 samples, together with an assessment of the error of each individual analysis. Figure 1 shows the loeation and average eadmium coneentration of eaeh of the major eolleetion points around the eoast. Samples 1-20 and sample 30 were eolleeted ln April 1976. The remaining samples were eolleeted in July 1976.

South coast region

Five samples were eolleeted near Albany in the Southern Oeean. The eoneentratlons at Mlddleton Bay and Frenehmans Bay in King George Sound are approximately half the values in the Inner Harbour at the Wharf and at Pelican Point. This eould be due to the presenee of cadmium in drainage from the Albany townsite, or aetivities at the wharf. The fifth sample

Table 1

Cadmium content of coastal water (in $\mu g\ kg^{-1}$ by weight)

Sample Number	Locality	Individual analyses	Mean concentration
	Albany		
1	Middleton Bay	0·060 ± 0·005 0·060 ± 0·006	0·060
2	Wharf	0·092 ± 0·004 0·101 ± 0·006	0·096
3	Pelican Point .	0·08 ± 0·01	0·08
4	Frenchmans Bay	0·031 ± 0·005 0·027 ± 0·008	0·029
5	Oyster Harbour	0·006 ± 0·004 0·005 ± 0·004	0·005
	Denmark		
6	Southern Ocean	0·024 ± 0·011 0·026 ± 0·004	0·025
7	Denmark River	0·003 ± 0·004 0·007 ± 0·004	0·005
8	*Yallingup* (ocean) .	0·017 ± 0·004 0·019 ± 0·004	0·018
9	*Dunsborough* (ocean)	0·022 ± 0·011 0·031 ± 0·014	0·026
10	*Busselton* (ocean)	0·032 ± 0·102 0·032 ± 0·006	0·032
11	*Bunbury* (ocean)	0·024 ± 0·003 0·020 ± 0·004	0·022
	Australind		
12	Collie River mouth	0·027 ± 0·004 0·035 ± 0·005	0·031
13	Pipeline	0·43 ± 0·01 0·35 ± 0·02	0·39
14	North of pipeline ...	0·189 ± 0·006 0·195 ± 0·007	0·192
	Cockburn Sound		
15	South Fremantle Power Station	0 030 ± 0·004 0·031 ± 0·004	0·030
16	Owen Anchorage ..	0·079 ± 0·005 0·070 ± 0·004	0·074
17	Southern Flats .	0·058 ± 0·005 0·068 ± 0·011	0·063
	Fremantle		
18	Inner Harhour	0·043 ± 0·004 0·049 ± 0·005	0·046
	Cottesloe Beach		
19	A	0·013 ± 0·006 0·014 ± 0·004 0·019 ± 0·004	0·016
20	B	0·015 ± 0·004 0·019 ± 0 004	
	Greenough		
21	Mid-river	0·047 ± 0·005 0·043 ± 0·004	0·045
22	Ocean (opposite river mouth)	0·21 ± 0·01 0·15 ± 0·01	0·18
23	Bore water	0·118 ± 0·006 0·125 ± 0·007	0·121
24	Tank water	0·090 ± 0·006 0·095 ± 0·008	0·092
25	*Kalbarri* (ocean)	0·03 ± 0·01	0·03
	Carnarvon		
26	Pelican Point (ocean)	0·017 ± 0·004 0·019 ± 0·004	0·018
27	Babbage Island	0·06 ± 0·01 0·043 ± 0·008	0·051
28	*Coral Bay* (ocean)	0·032 ± 0·009 0·026 ± 0·008	0·029
29	*Exmouth Gulf* (ocean)	0·16 ± 0·01 0·14 ± 0·01	0·15
30	*Pardoo Station* (ocean)	0·129 ± 0·006 0·132 ± 0·007	0·130

was collected just south of the King River Bridge in Oyster Harbour. The concentration of 0.005 ppb is extremely low and probably reflects the fact that two rivers—the King and the Kalgan—flowing into this inlet probably have low cadmium levels. Rosman and De Laeter (1977) showed that the cadmium concentration of water in the Swan and Peel inlet river systems could be as low as 0.01 ppb. Two samples were also analysed at Denmark, a small town some 54 km west of Albany. One sample was taken from the ocean, the second from the Denmark River. The results were almost identical to the corresponding types of collection points at Albany.

Southwest coast region

The cadmium contents of ocean water at four collection sites along some 90 km of coastline from Yallingup to Bunbury in the Indian Ocean gave extremely low and consistant values from 0.018 to 0.032 ppb, which are similar to the cadmium values for the Southern Ocean samples.

The three Australind samples were collected in Leschenault Inlet, a large, tidal inlet with an opening to the ocean at the southern end, near the town of Bunbury. The Collie River enters the inlet approximately 2 km north of the outlet. A titanium-ilmenite refinery is located about 5 km from the channel on the landward side of the inlet. Effluent from the factory is carried across the inlet to the ocean by an elevated pipeline. The sample from the mouth of the Collie River gave a cadmium value of 0.031 ppb. This low value is probably due to the fresh water flowing down the river, together with the muddy nature of the river mouth which acts as a sink for the cadmium. The second sample was taken directly under the raised centre section of the pipeline. This section is continually leaking effluent, and the cadmium content of 0.39 ppb was the highest value found in any of the 30 samples analysed. The third sample was taken approximately 3 km to the north of the pipeline. The cadmium content of 0.192 ppb was still high, but approximately half the value of the pipeline sample. There are strong tides in the estuary which would disperse the cadmium from the effluent throughout the estuary, although the sediments in the inlet would undoubtedly act as a sink for cadmium as occurs in the Peel Inlet some 100 km to the north of the Leschenault Inlet (Rosman and De Laeter 1977).

Fremantle region

Three samples were taken from Cockburn Sound which has a complex system of tides, currents and wind effects. Industry along Cockburn Sound releases effluent at a number of places, and Meagher and Le Provost (1971) have measured zinc concentrations at the 50-1 000 ppm level in a number of locations in the Sound. The first sample was collected approximately 1 km offshore from the South Fremantle Power Station. The second sample was collected off Southern Flats approximately 1 km east of Careening Bay (Garden Island). The third was collected approximately 1 km offshore from Woodman Point at Owen Anchorage. All three samples gave reasonably low values—and all were significantly lower than the values measured in Leschenault Inlet.

The cadmium content of the water sample collected in Fremantle Harbour gave a value of 0.046 ppb which compares reasonably well with the value of 0.06 ppb collected at the Fremantle Traffic Bridge in April 1975 as reported by Rosman and De Laeter (1977). Two samples were collected off Cottesloe Beach, the first sample being analysed on three, and the second sample on two separate occasions. The results give a good indication of the reproducibility and precision of the isotope dilution technique for sea water samples.

The Cottesloe samples were analysed over a three month period, and the consistency of the results supports the conclusion of Shendrikar *et al.* (1975), that absorption of cadmium on high density polyethylene is minimal, even over an extended period of time.

North coastal region

Four samples were collected at Greenough, some 8 km south of Geraldton. The Grecnough area is a flat, open expanse of agricultural land through which the Greenough River flows. Across the mouth of the river is a semi-permanent sand bar about 200 m wide. In periods of heavy rainfall the river floods over a considerable land area and breaks the sand bar. However, in seasons of low rainfall the additional water is lost by seepage without actually breaking the bar.

The cadmium concentration at a point in the river approximately 130 m upstream from the mouth was 0.045 ppb. In seawater directly opposite the river mouth, the concentration was 0.18 ppb. A sample of water taken from a bore 30 m deep 250 m north of the river mouth gave a value of 0.121 ppb. Another sample taken from a galvanized iron tank fed from the bore but diluted by fresh water, gave a value of 0.092 ppb. The sandy soil in the vicinity of the river mouth does not absorb cadmium to any extent, whereas the rich humic material in the river is a good absorber of cadmium (Rosman and De Laeter 1977). The cadmium concentrations at Greenough therefore seem to be the result of absorption and seepage mechanisms.

The concentration of cadmium in the sea water at Kalbarri at the mouth of the Murchison River, was 0.03 ppb. The Murchison River is open to the sea and drains a large agricultural area including a mineraliferous zone east of the National Park. The Carnarvon samples were collected in the ocean at Pelican Point and in the estuary of the Gascoyne River near Babbage Island. The cadmium concentrations of 0.018 and 0.051 ppb respectively are typical of coastal and estuarine waters in Western Australia.

Coral Bay, approximately 200 km north of Carnarvon, is a reef-locked bay which is not linked to any river system. A small settlement at the location is used by holiday makers. The cadmium concentration of 0.029 ppb is significantly less than the water sample taken in

Exmouth Gulf near the Exmouth townsite. The concentration here was 0.15 ppb and probably reflects the proximity of the town and the activities at the U.S. Naval Supply Depot which serves the North West Cape radio base.

The most northerly sample was collected off the coast at Pardoo Station, approximately 100 km northeast of Port Hedland. The cadmium concentration of 0.13 ppb was higher than expected at this very remote locality.

Conclusions

This study has shown that it is difficult to establish definite base-line levels for cadmium in coastal sea water, even for a relatively uninhabited area such as Western Australia. The concentration of cadmium is obviously influenced to a significant extent by industry, agriculture, estuaries and river systems. The nature of the sediment underlying the locality is also a significant factor governing the amount of cadmium in the marine environment. Remote localities which are not near rivers and have sandy sediments, show the lowest concentrations of cadmium. From these localities one can estimate a base-line concentration of 0.013 ppb cadmium for coastal sea water, and the higher values can therefore be compared to this base-line value. The highest cadmium concentration was found at Australind, and this is probably due to effluent from the ilmenite works nearby. On the other hand the cadmium values in Cockburn Sound are significantly lower, and show little evidence of industrial contamination. In fact sea water samples collected near Grecnough, Exmouth and Pardoo Station show cadmium concentrations that are approximately twice as large as the highest reading found in the Cockburn Sound area.

Preston (1973) has given the results of a study of heavy metal concentrations in British coastal waters conducted in 1969-1970. Samples were collected in five coastal areas and gave cadmium concentrations from <0.01 to 0.11 ppb. Preston (1973) concludes that elevated concentrations of heavy metals are largely restricted to estuaries and the coastal margin, and are associated with drainage from industrial areas or the dumping of sewerage sludge and industrial wastes. These conclusions are also applicable to the Pacific, Gulf and Atlantic coasts of the United States (IDOE 1972).

This study has shown that the stable isotope dilution technique is an excellent method of measuring the concentrations of cadmium with reasonable accuracy at the levels typically found in sea water. The present study complements the overseas data for cadmium concentrations in coastal waters for the eastern seaboard of the Indian Ocean, and part of the Southern Ocean.

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